

Communication

Catalytic activity of N-heterocyclic carbenes in ring opening polymerization of cyclic siloxanes

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Abstract

Taking advantage of the strong nucleophilic properties of N-heterocyclic carbene (NHC), the efficient catalytic ring opening polymerization (ROP) of cyclotetrasiloxane D₄ was achieved under mild conditions.

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1. Introduction

The transformation of organic compounds catalyzed by neutral organic molecules is becoming a very important research area due to the significant structural diversity possible for the catalysts, the mild reaction conditions employed, their low cost and the absence of metal contaminant [1]. The use of stable strongly σ -electron donating N-heterocyclic carbenes (NHCs) [2] not only as ligands for the preparation of organometallic catalysts [3] but on their own as organic catalysts [4] has grown considerably [5–9]. Hedrick et al. recently reported a well-controlled ring opening polymerization (ROP) of cyclic esters using NHC catalysts [10], which is one of the very few organocatalytic systems known for nucleophilic ROP [11].

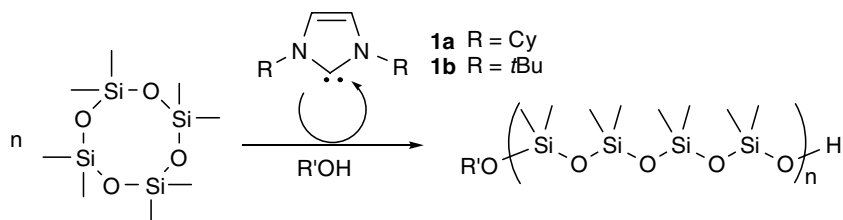
Since all the reported catalytic reactions initiated by NHCs involve the transformations of carbonyl compounds, we decided to expand the scope of this family of organocatalytic systems to inorganic polymerization. Polymeric siloxanes such as poly(dimethylsiloxane) (PDMS) are

very important materials because of their unique properties that are attractive for many industrial applications [12]. Recently, two new systems combining an alcohol and phosphazene [13] or phosphorus ylide [14] bases were shown to be extremely fast initiators in the ROP of cyclic siloxanes. Indeed, these strong bases react readily with alcohols to generate alcoholates with very soft and voluminous organic counterions that confer high solubility and an inherently low tendency for ion-pair association which enhances the initiation and propagation steps. Although they are very efficient initiators, they are not catalysts for the process. We herein report that N-heterocyclic carbenes, such as **1a**, are efficient catalysts for the ROP of cyclotetrasiloxane D₄ (Scheme 1).

2. Results and discussion

Polymerization reactions were carried out by adding, to a mixture of D₄ and alcohol initiator (three types of alcohol were surveyed), a filtered THF solution of NHC **1a** (0.2 M), which was prepared by the deprotonation of the corresponding imidazolium triflate with potassium hexamethyldisilazide (KHMDS) [15]. After heating the mixture at

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Scheme 1. ROP of D_4 catalyzed by NHC **1a,b**.

80 °C for 16 h, GPC analysis of the resulting polymers obtained showed that the monomer conversions were around 85% in all cases (Table 1).

The catalytic properties of **1a** were clearly indicated by the gradual reduction of the molecular weight of polysiloxanes with increasing the quantity of initiator relative to that of **1a**. From these data it is clear that more efficient molecular weight control is obtained using primary alcohols (MeOH and BnOH), as indicated by the inverse dependence of molecular weight upon the amount of alcohol used. In the case of the hindered *t*-BuOH, only a slight decrease in molecular weights was observed, even in the presence of a large excess of the initiator. These observations are consistent with the less hindered alcohols provid-

ing a fast initiation step compared with the propagation step, which results in a more efficient catalytic system.

In order to rule out the possibility that small residual traces of trifluoromethanesulfonate salts were initiating ROP, polymerization tests were carried out using purified NHCs [crystallized **1a**, or sublimed **1b** ($R = t\text{-Bu}$)] [16], and benzyl alcohol as initiator. Exactly the same trends were observed as those reported in Table 1, which strongly support the catalytic role of the NHC for the ROP of D_4 (Table 2).

Furthermore, the nucleophilicity of the NHC is intimately linked to catalytic activity. Indeed NHC **1c** ($R = \text{mesityl}$) with bulky and π -accepting substituents on the nitrogen atoms is no longer active for the polymerization of D_4 .

Table 1
Results of ROP of D_4 catalyzed by **1a** with different types of alcohols: [cat.] = 1000 ppm, 80 °C, 16 h

Initiator	<i>t</i> -BuOH		MeOH ^b		BnOH	
	$M_n [10^3]$	I_p^a	$M_n [10^3]$	I_p^a	$M_n [10^3]$	I_p^a
1	216	1.59	218	1.64	211	1.65
3	190	1.64	164	1.61	157	1.70
5	146	1.61	128	1.61	125	1.61
10	144	1.62	122	1.54	75	1.56
20	138	1.58	72	1.53	49	1.68
70	114	1.59	28	1.53	17	1.53

^a Polydispersity index.

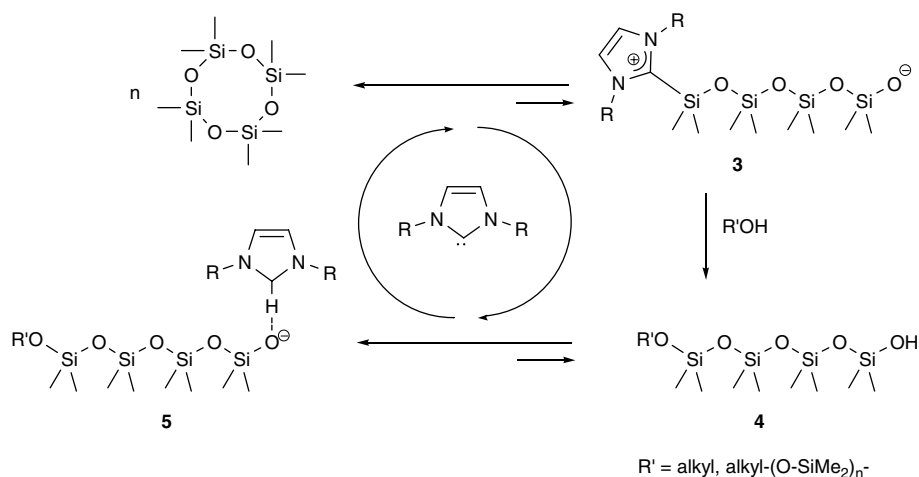
^b 50 °C, 16 h.

Table 2
Results of ROP of D_4 using purified NHCs (**1a,b**): I = BnOH, [cat.] = 1000 ppm, 80 °C, 16 h.

[I]/[cat.]	1a ^a			1b ^b		
	1	5	20	1	5	20
$M_n (10^3)$	186	98	61	161	114	47
$M_w (10^3)$	304	150	91	266	183	74
I_p	1.63	1.53	1.48	1.65	1.61	1.57
Yield	85	86	85	88	88	87

^a Purified by recrystallization in pentane.

^b Purified by sublimation.



$R' = \text{alkyl, alkyl-(O-SiMe}_2\text{)}_n\text{-}$

Scheme 2. Proposed mechanism of ROP of D_4 .

The polymerization reaction can be realized easily quenched by heating (150 °C, 5 h) the resulting polymer which decomposes the NHC catalyst. Without this treatment, the carbene catalyst remains active.

From a mechanistic point of view, a similar process to the ROP of cyclic esters proposed by Hedrick et al. can be considered here. Polymerization is initiated by nucleophilic attack of the NHC at the silicon centre of D₄ inducing ring opening of the cyclosiloxane monomer and subsequent formation of the zwitter-ionic silonate **3**, which reacts with alcohol initiator to form silanol **4** (Scheme 2).

This proposed mechanism is consistent with the susceptibility of the initiation step upon the nucleophilicity and steric bulk of the NHC catalyst, and the necessity for an alcohol initiator. Analysis of the polymer endgroups confirmed the initiation by alcohols. Indeed, signals characteristic of –SiMe₂OH and –SiMe₂OBn endgroups were observed in the ²⁹Si NMR spectrum at –11 and –12 ppm, respectively [17]. Moreover, kinetic studies show that the polymerization is sensitive to the amount of NHC catalyst (Fig. 1). Under the stoichiometric conditions ([I]/[cat.] = 1) the polymerization is extremely fast with 3000 ppm compared to 500 ppm of NHC **1a**.

The fact that the rate of the polymerization is only accelerated by increasing the amount of NHC, and not on increasing the amount the alcohol, suggests that the rate-determining-step could be the nucleophilic attack of the NHC on D₄. Interestingly, the use of an excess of BnOH initiator slows down the polymerization reaction rate, in

agreement with the deactivation of NHC catalyst **1** by reprotonation with the excess of alcohol or by forming more acidic silanols **4** [18]. However, all attempts to observe the NHC–D₄ adduct **3** failed (Scheme 3).

3. Conclusion

In conclusion, the nucleophilicity of NHC **1a** can be exploited to bring about the first efficient catalytic ROP of cyclotetrasiloxane D₄, which was achieved under mild conditions. Interestingly, with this NHC/ROH system the molecular weight of the silicone polymers can be regulated simply by varying the quantity of the alcohol initiator. Because of the neutral condition, the only by-products are a catalytic amount of moisture sensitive NHC and volatile alcohol which can be easily removed. Detailed mechanistic studies of this new ROP and the use of other stable singlet carbenes are under active investigation.

4. Experimental

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. D₄ was dried by azeotropic distillation with small amount of toluene and was kept over 4 Å molecular sieves. *t*-BuOH, MeOH and BnOH were dried under Ar by distillation over small amount of Na metal. ¹H, ¹³C and ²⁹Si NMR spectra were recorded on Bruker AC200, WM250 or Avance 300 spectrometers. ¹H, ¹³C and ²⁹Si NMR chemical shift were reported in ppm relative to Me₄Si as external standard. D₄ was obtained from Rhodia Silicones. NHCs (**1b**, **1c**) were prepared according to a previously reported method.

The degree of conversion and molecular weight distributions were obtained from gel-permeation chromatography (GPC) using an HP 1050 Series instrument. The instrument was fitted with two Waters styragel HR GPC columns (7.8 × 300 mm, HR4 and HR4E) heated to 35 °C. Toluene was used as the eluent. Sample detection was performed at 35 °C by a Waters 410 differential refractometer. The molecular weights of the silicones prepared are uncorrected and reported relative to the polystyrene standards (Polymer Laboratories) used for calibration.

4.1. Synthesis of NHC (R = Cy) (**1a**)

To a solid mixture of imidazolium triflate (1.5 g, 3.9 mmol) and potassium *t*-butoxide (0.44 g, 3.9 mmol) was added at –78 °C 5 mL of THF. The solution was then stirred at RT for 1 h. After removal of the potassium salts by filtration, and removal of THF under vacuum, the residue was extracted with pentane. Carbene **1a** was obtained as colourless crystals from a concentrated pentane solution at –30 °C (yield, 0.59 g, 65%). Mp 56–57 °C. ¹H (C₆D₆, 300 MHz): δ = 0.9–1.4 (m, 6H; CH₂), 1.5–1.65 (m, 2H; CH₂), 1.65–1.9 (m, 8H; CH₂), 2.1–2.3 (m, 4H; CH₂), 4.22 (tt, *J* = 3.7 Hz, *J* = 11.7 Hz, 2H; NCH), 6.73 (s, 2 H;

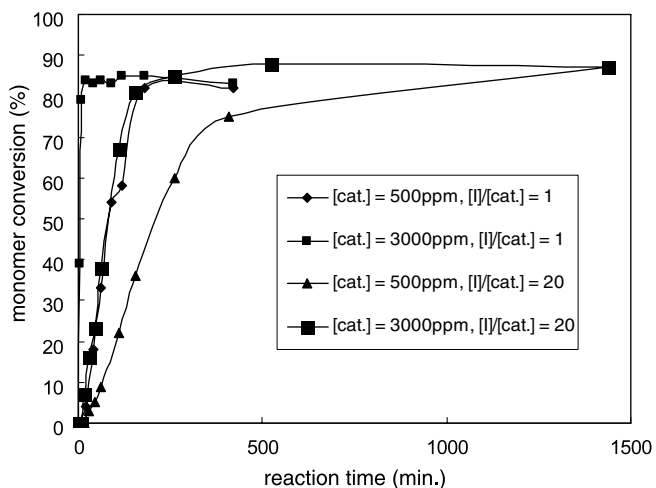
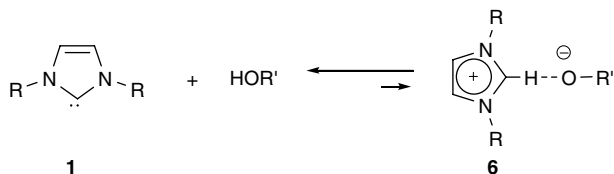


Fig. 1. Reaction time vs. % monomer conversion; [cat.] = 500 ppm or 3000 ppm. cat. = **1a**, I = BnOH, [I]/[cat.] = 1 or 20, 80 °C.



Scheme 3. Acid/base equilibrium of NHC and alcohols.

HC=CH). ^{13}C (C_6D_6 , 75 MHz): $\delta = 24.9$ (s; CH_2), 25.1 (s; CH_2), 34.3 (s; CH_2), 59.1 (s; NCH), 115.0 (s; $\text{C}=\text{C}$), 211.3 (s broad; NCN).

4.2. Typical procedures for D_4 polymerization

Method A: To a mixture of two solids, imidazolium triflate (0.38 g, 1 mmol) and potassium hexamethyldisilazide (0.20 g, 1 mmol) was added, at RT, 5 mL of THF. The formation of carbene **1a** was monitored by ^1H and ^{13}C NMR spectroscopies. After removal of KOTf by filtration, a THF solution of **1a** was obtained. To a THF solution of **1a** (0.2 M) were added at RT the appropriate quantities of D_4 and alcohol. Then the mixture was heated at 80°C for 16 h. **Method B:** To purified NHC in the solid state (**1a** or **1b**) were added, at RT, the appropriate quantities of D_4 and alcohol. Then the mixture was heated at 80°C for 16 h. In both cases, the obtained silicones were analyzed by ^1H NMR and gel-permeation chromatography (GPC) without any treatments.

Acknowledgements

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